6 ACIDIFICATION

One of the primary objectives of the 1995-1997 Maryland Biological Stream Survey (MBSS or Survey) is to assess the effect of acidic deposition on the biological resources of Maryland streams. Acidification is known to have detrimental effects on fish and other aquatic biota (Baker and Christensen 1991), both from direct effects of low pH and through toxic effects resulting from increases in heavy metal concentrations (e.g., aluminum and mercury) that leach from the soils. Because the Survey collects both biological and water chemistry data, it has the ability to measure not only the extent of acidification in Maryland but also the extent of potential impacts on aquatic biological communities. This chapter examines statistical relationships between acidification and biological condition in benthic macroinvertebrate, fish, and amphibian and reptile communities.

6.1 BACKGROUND

The effects of acidic deposition on stream chemistry are well documented. Maryland's 1987 Synoptic Stream Chemistry Survey (MSSCS; Knapp et al. 1988) concluded that approximately one-third of all headwater streams in Maryland are sensitive to acidification or are already acidic. Research has demonstrated that the vulnerability of stream systems to acidic deposition depends on watershed hydrology and the ability of the vegetation, soils, and bedrock within the watershed to buffer acidic inputs.

The defining characteristics of surface waters sensitive to acidification are low to moderate pH and acid neutralizing capacity (ANC). pH is a measure of the acid balance of a stream. The pH scale ranges from 0 to 14, with pH 7 as neutral. Low to moderate pH ($\leq$ 6) signifies high acidity. ANC is a measure of the capacity of dissolved constituents in the water to react with and neutralize acids and is used as an index of the sensitivity of surface water to acidification. The higher the ANC, the more acid a system can assimilate before experiencing a decrease in pH. Repeated additions of acidic materials can cause a decrease in ANC. In many acidic deposition studies (e.g., Schindler 1988), an ANC of 200 μeq/l is considered the threshold for defining acid-sensitive streams and lakes.

Alternatively, a stream's sensitivity to acid deposition can be measured using "indicator organisms" that are selected as representatives of community health. In a recent study of acid deposition impacts in Maryland streams (Janicki et al. 1991), the sensitivity of an indicator species was expressed as the critical pH at which half or more of the population experiences acute or chronic effects. The level of acid deposition which results in the critical pH is known as the "critical load." In the critical loads study, information on soil buffering ability was combined with MSSCS ANC values to estimate critical loads at specific sites across the state. Critical load results revealed wide differences in the sensitivity of Maryland streams in different provinces:

- The Appalachian Plateau, Coastal Plain and portions of the Blue Ridge are very sensitive (critical load values < 0.5 keq SO_4/ha/year or 24 kg SO_4/ha/year).
- In contrast, the Valley and Ridge, Piedmont, and portions of the Blue Ridge regions exhibit critical loads well over 2.0 keq SO_4/ha/year (96 kg SO_4/ha/year). These are areas where limestone bedrock and derived soils are prevalent.

These critical loads values provided the basis for a reassessment of acidic deposition in 1998 (Miller et al. 1998). When measured sulfate deposition was compared with critical loads, the results suggested that streams continue to be impacted in some areas of the State despite recent reductions in industrial sulfate emissions, a finding consistent with stream chemistry measured in the 1995-1997 MBSS.

Acidification is known to cause declines in both the diversity and abundance of fish populations. Current evidence indicates that the number of aquatic taxa in an ecosystem usually declines with increasing acidity (Eilers et al. 1984, Mills and Schindler 1986, Stephenson and Mackie 1986). In a review of pH effects on aquatic biota, Baker and Christensen (1991) report a number of critical thresholds at which certain fish populations are affected. Many streams in Maryland have pH values below critical levels, with critical pH values for inland species ranging from 5.0 to 6.5 (Baker et al. 1990a; Morgan et al. 1991). For instance, several bass and trout species have a reported critical threshold of pH 5.0-5.5, while a number of more sensitive cyprinid and darter species are adversely affected at pH 5.5-6.0. Acid-tolerant species, such as the yellow perch *(Perca flavescens),* can survive at pH levels of 4.5 or lower. Eastern mudminnow (*Umbra pygmaea*) have been found in waters with pH 4.0 or lower (Jenkins and Burkhead 1993).

The primary mechanisms for fish population declines under acidic conditions include both recruitment failure (owing to increased mortality of early life stages) and direct effects on adult survival. One of the physiological effects observed when pH decreases is the disruption of the normal internal ionic salt balance, which causes the fish to lose salt to the surrounding water. If the salt losses exceed intake, fish go into shock, lose equilibrium and eventually die. Acidic waters can also inhibit the development of fish reproductive organs and facilitate the development of a mucous that suffocates eggs and fry (Eno and Di Silvestro 1985). The loss of entire fish populations in abnormally acidic streams or lakes usually occurs because of successive failures in the reproductive cycle. Other detrimental effects are caused by the increased concentrations of metal ions that result from acidification (e.g., from the leaching of aluminum and the formation of methylmercury).

In addition to potential long-term (chronic) acidification, streams in Maryland are susceptible to rapid, short-term increases in acidity (episodic acidification) related to precipitation, snow melt, and stormflow events (Greening et al. 1989; Gerritsen et al. 1992; Wigington et al. 1993). One study estimates that 50% more streams in the northern Appalachian Plateau of Western Maryland probably experience the deleterious effects of episodic acidification than are chronically acidified (Eshleman 1995). Spatial and temporal variability of acidic conditions are important to the magnitude of effects on aquatic biota. For example, a pulse of episodic acidification during juvenile recruitment could have a greater effect on a fish population than it would at other times of the year. The highest levels of acidity in Maryland streams have been recorded in the spring, when many fish, including economically important anadromous fish species of the Chesapeake Bay, enter the freshwater portions of coastal streams to spawn. Large-scale fish kills frequently result when snow melts and large quantities of acidic materials are released into rivers and streams (Eno and Di Silvestro 1985).

Because many invertebrate taxa are also sensitive to acidification, detrimental effects on food webs may occur well before direct toxicity to fish is evident (Schindler et al. 1989, Gill 1993). Benthic invertebrate taxa richness may be reduced as a result of acidification (Ford 1988). Often some taxa are lost as a result of acidity, but this loss may be compensated for by an increase in numbers of acid-tolerant species, resulting in little or no decrease in overall biomass (Eriksson et al. 1980, Dixit and Smol 1989). Several invertebrate taxa— notably mollusks, crustaceans, leeches, mayflies, some species of water striders, caddisflies, damselflies, dragonflies, and cladocerans— are sensitive to acidification and become scarce or disappear between pH 5.0 and 6.0 (Havas and Hutchinson 1982, Eilers et al. 1984, Raddum and Fjelheim 1984, Ormerod and Tyler 1986, Bendell 1988, Bendell and McNicol 1987).

The Survey provides an opportunity to examine the influences of acidic deposition on fishes and other biota in non-tidal streams. Results from the 1995-1997 MBSS sampling are presented below.

6.2 EXTENT OF THE ACIDIFICATION PROBLEM

6.2.1 Low pH

In evaluating the influence of acidification on stream biological communities, it is important to determine the extent and distribution of acidic and acid-sensitive streams. During spring sampling, an estimated 2.6% of the stream miles across the 17 basins sampled in the 1995-1997 MBSS had pH less than 5, while another 6.4% had pH 5-6 (Figure 6-1). Low spring pH was most common in the Pocomoke basin, where about 34% of stream miles had pH less than 5 and 28% of stream miles had pH 5-6. Summer field sampling results were similar: across the 17 basins an estimated 1.8% of the stream miles had pH less than 5, while 4.1% had pH 5-6. Of the 17 basins sampled in the MBSS, 10 experienced low pH during summer sampling and 13 did during spring sampling. The lowest summer pH was observed in the North Branch Potomac basin, where about 16% of the stream miles had summer pH less than 5 and 1% had summer pH 5-6 (Figure 6-2).

Small streams, particularly first-order streams, appeared to be most susceptible to low pH conditions, with the highest percentage of stream miles in the low pH classes. None of the third-order sites sampled had spring pH < 5. During spring, only 2.7% of third-order stream miles had pH 5-6, compared to 8.4% of first-order stream miles. Likewise, only 1.6% of third-order stream miles sampled in summer had pH <6, compared to 7.3% of first-order stream miles.

6.2.2 Low Acid Neutralizing Capacity (ANC)

Although pH is the most commonly used measure of acidification, ANC is a better overall measure of acidification and acid sensitivity, because it also indicates which systems are likely to become acidified under episodic conditions. The following critical ANC values were used to characterize streams according to acid sensitivity: < 0 μeq/l (acidic), $0 \leq \text{ANC} < 50$ μeq/l (highly sensitive to acidification), $50 \leq \text{ANC} < 200$ μeq/l (sensitive to acidification), and ≥ 200 μeq/l (not sensitive to

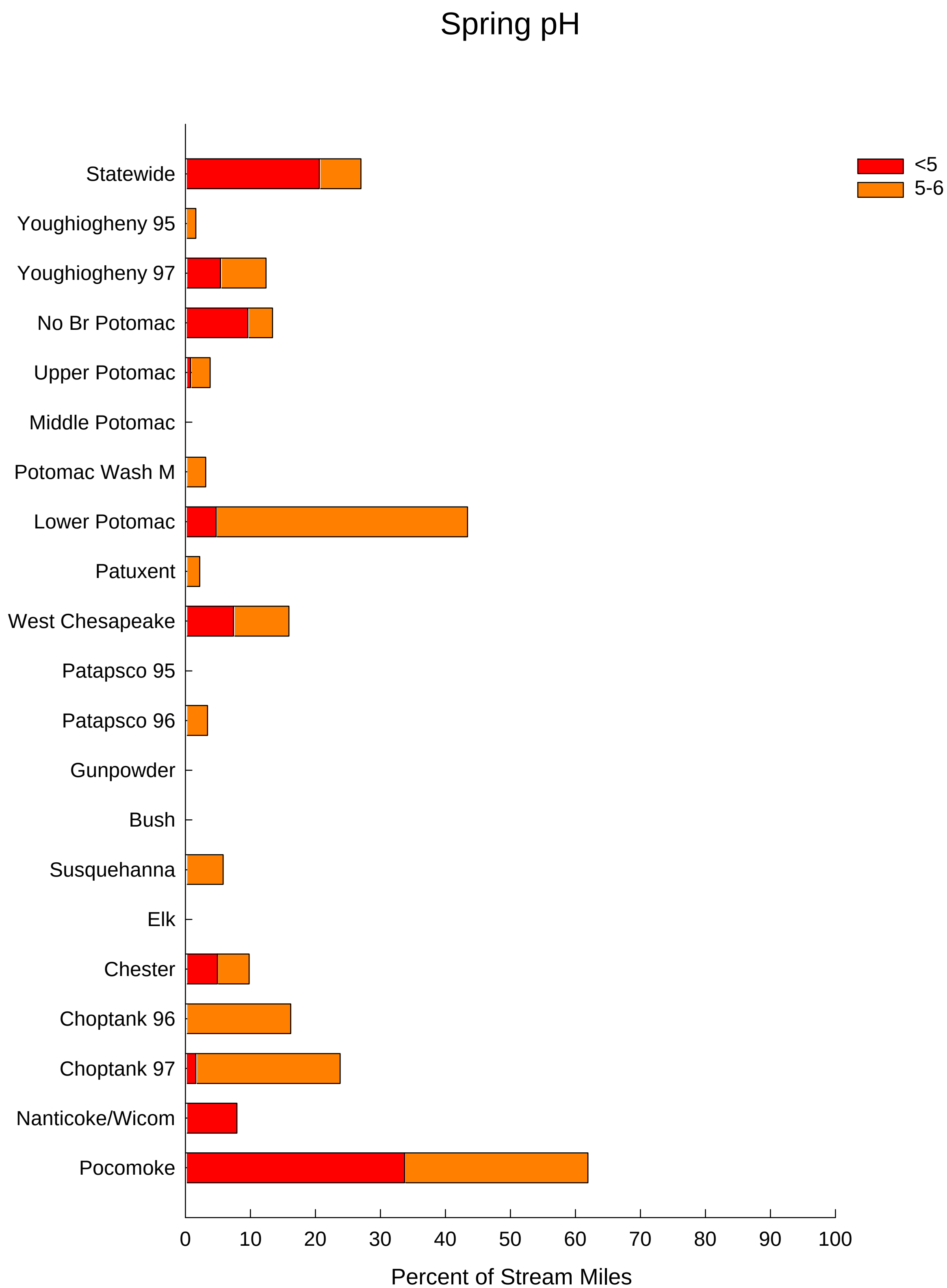

Figure 6-1. Percentage of stream miles with low pH by basin (spring pH), for basins sampled in the 1995-1997 MBSS

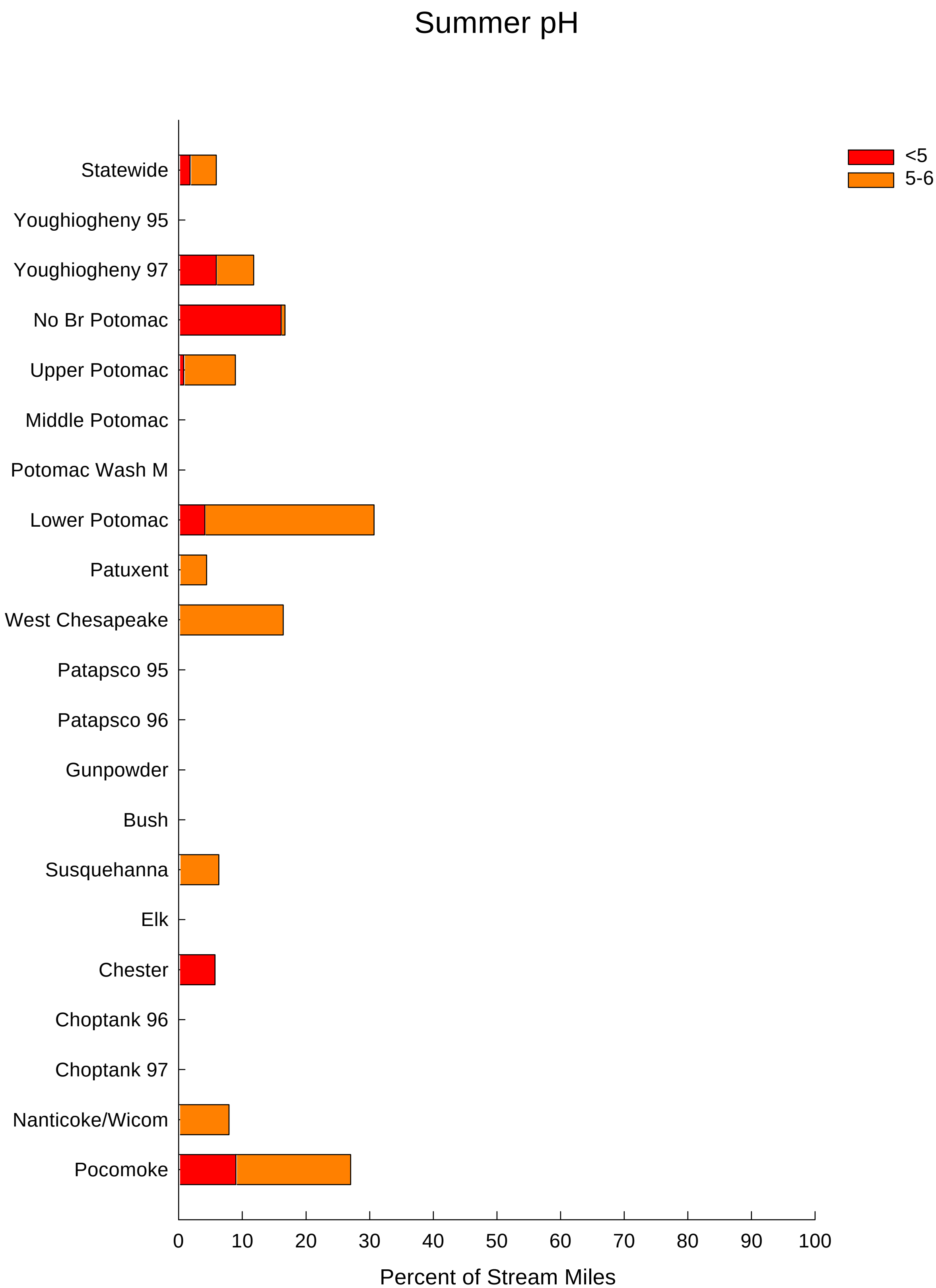

Figure 6-2. Percentage of stream miles with low pH by basin (summer pH), for basins sampled in the 1995-1997 MBSS

acidification). A number of questions about stream acidification can be answered with MBSS results. Statewide, an estimated 28% of the stream miles were acidic or acid-sensitive, including about 2% acidic, 4% highly sensitive, and 22% sensitive to acidification. Five basins had greater than 50% of stream miles with ANC < 200: the Lower Potomac (79%), Pocomoke (66%), North Branch Potomac (64%), Youghiogheny (63% in 1997 sampling), and Choptank (62% in 1996 sampling). The Susquehanna and Patapsco basins had no sites with ANC < 200. The percentage of acid sensitive, highly sensitive, and acidified stream miles in each basin is shown in Figure 6-3.

Statewide, the estimated percentage of stream miles with ANC < 0 was 3% of first-order stream miles, 2% of second-order, and 0% of third-order stream miles. The estimated percentage of stream miles with ANC < 200 was 31% of first-order, 21% of second-order, and 20% of third-order stream miles.

6.3 SOURCES OF ACIDITY

In estimating the extent of acidification of Maryland streams, it is important to understand how acidic deposition, acid mine drainage, agricultural runoff, and natural organic materials contribute to the observed acidification. Acidic deposition is the contribution of material from atmospheric sources, both as precipitation (wet) and particulate (dry) deposition. Acidic deposition is generally associated with elevated concentrations of sulfate and nitrate in precipitation. Acid mine drainage (AMD) results from the oxidation of iron and sulfur from mine spoils and abandoned mine shafts and is known to cause extreme acidification of surface waters. Streams strongly impacted by AMD exhibit high levels of sulfate, manganese, iron, and conductivity. A third source of acidification is surface runoff from agricultural lands that are fertilized with high levels of nitrogen or other acidifying compounds. Lastly, the natural decay of organic materials may contribute acidity in the form of organic anions, as in blackwater streams associated with bald cypress wetlands. Streams dominated by organic sources of acidity are often characterized by high concentrations of dissolved organic carbon (DOC > 8 mg/l) and organic anions. Water chemistry data may be analyzed to distinguish among the four sources of acidity potentially affecting sites in the 17 basins sampled in the 1995-1997 MBSS.

Sources of acidification in Maryland streams have been examined in previous DNR studies using water chemistry data from the MSSCS and other regional surveys. In a study of Maryland Coastal Plain streams, Janicki (1991) reported a predominance of low ANC conditions and found that differences in stream chemistry within the region were related to land use. In particular, ANC tended to be higher in watersheds dominated by agriculture. Agricultural activities in Coastal Plain watersheds can have different effects on stream chemistry, adding both ANC (from soil liming practices) and strong acid anions (from nitrogen fertilizers) (Janicki et al. 1995). Janicki and Wilson (1994) estimated that acidic deposition was the dominant source of acidity in about 45% of the low ANC streams in the Maryland Coastal Plain, while combined inputs from acidic deposition and agricultural sources affected about 55% of the streams. In Maryland's Appalachian Plateau and Blue Ridge regions, where there are also a significant number of acidic and acid-sensitive streams, bedrock geology was an important factor in determining stream response to acidic deposition, according to analyses by Janicki (1995). Atmospheric deposition was identified as the major source of acidification in the Appalachian Plateau and Blue Ridge streams. Organic acids and agricultural sources did not appear to be major contributors to acidification in Western Maryland streams. The analyses by Janicki (1995) did not include effects of acid mine drainage.

For the MBSS, a new analysis was conducted to estimate the extent of impacts by acidic deposition, acid mine drainage, agricultural runoff and organic sources. Water chemistry data from sites with low ANC (< 200 μeq/l) were examined to identify dominant sources of acidification (Figure 6-4) and to estimate the percentage of stream miles impacted by each. Results were compared by river basin, because different acidity sources were expected to be important in the eastern and western parts of the State.

Instream concentrations of sulfate and nitrate ions are important indicators of acid sources. For areas near the ocean, however, analyses of stream chemistry need to account for contributions of sulfates from airborne sea salts. In our analysis, measured instream sulfate concentrations were corrected for sea salt influence, which decreases with distance from the coast. The amount of marine sulfate is related to levels of marine chloride, which can be estimated from a site's distance from the coast. Because the MBSS does not directly measure chloride concentrations, estimates of sea salt sulfate and chloride concentrations were made using the following relationships derived for Mid-Atlantic streams by the National Stream Survey (Baker et al. 1990b, Kaufmann et al. 1992):

$$\ln(Cl^-_{sea}) = 5.4328 - 0.0180*Dist + 0.00004*Dist^2$$

$$\text{sea salt corrected } SO_4 = SO_4^{2-}{}_{(observed)} - 0.013*Cl^-_{sea}$$

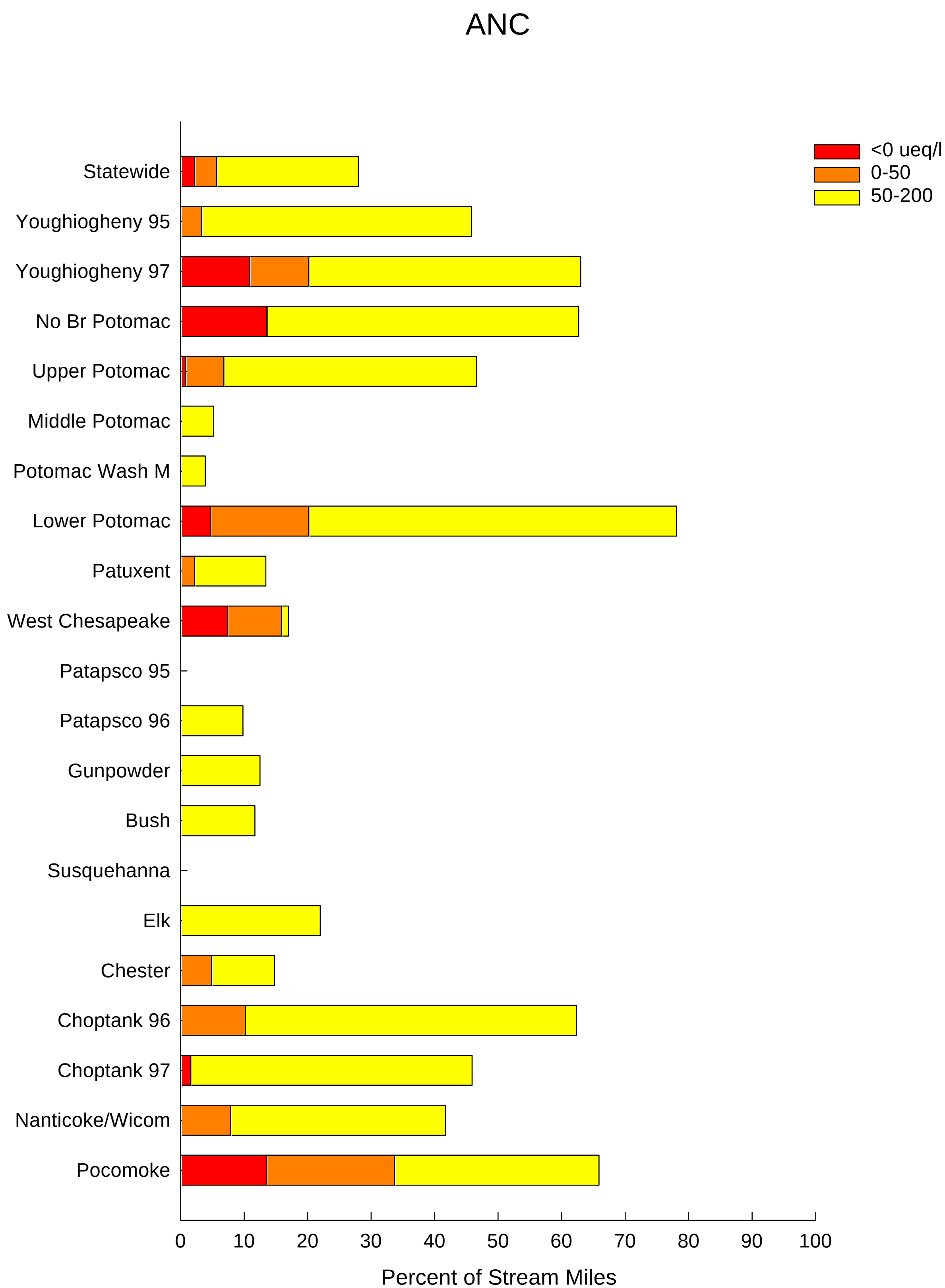

Figure 6-3. Percentage of stream miles with low ANC by basin, for basins sampled in the 1995-1997 MBSS. ANC classes are in μeq/l.

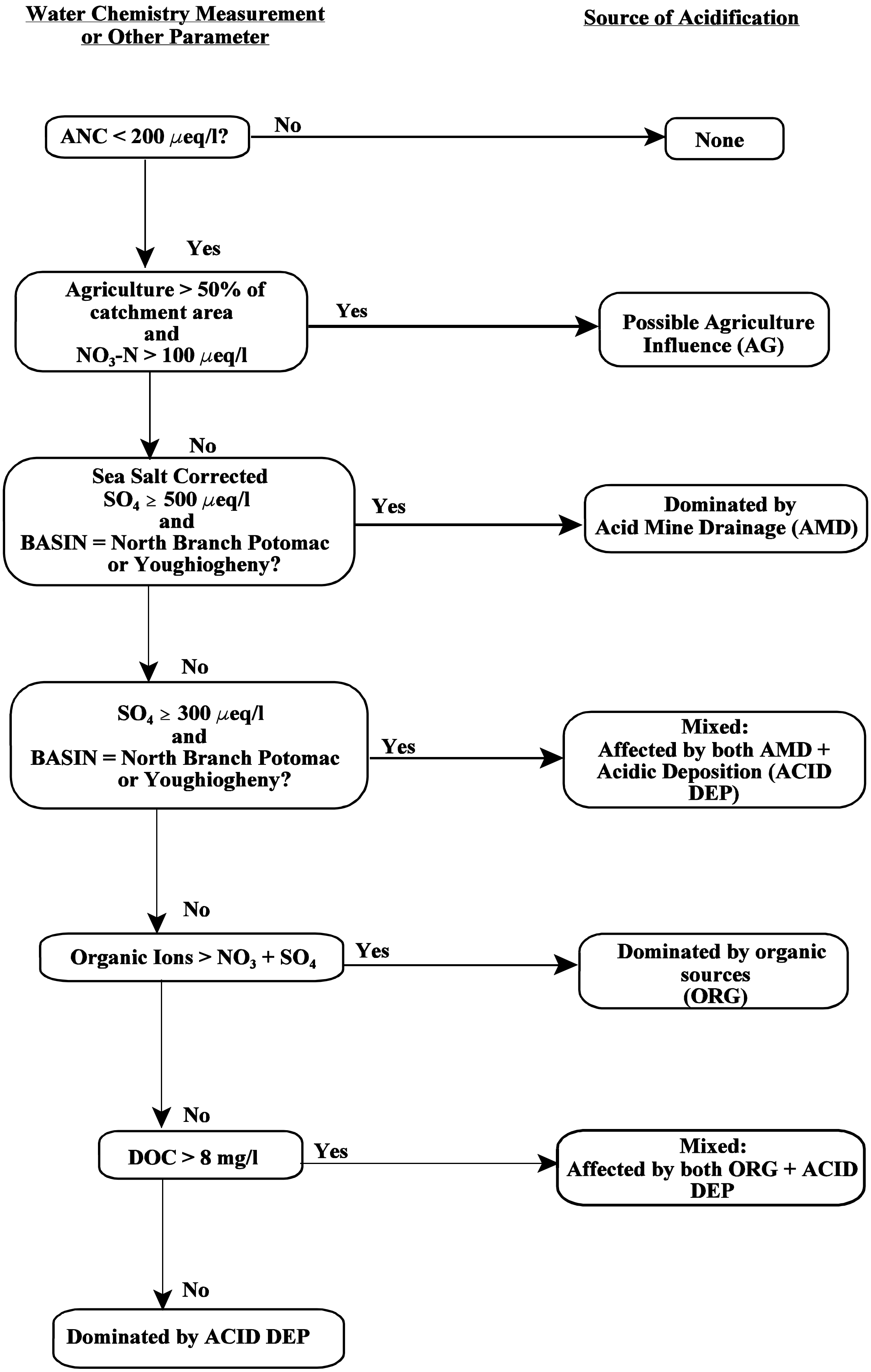

Figure 6-4. Procedure for the determination of acid sources for sites sampled in the 1995-1997 MBSS

where Cl^-_{sea} = concentration of sea salt derived chloride (μeq/l), Dist = distance from the coast (km), and $SO_4^{2-}{}_{(observed)}$ = observed sulfate concentration (μeq/l). The sea salt correction was made only for MBSS sites within 200 km of the ocean. Beyond 200 km, streams are assumed to have no sea salt contributions (Baker et al. 1990b).

In Western Maryland streams, sulfate concentrations were used to distinguish MBSS sites having AMD as the dominant source of acidification from those dominated by acidic deposition. Based on results of previous studies in Mid-Atlantic Highlands streams (Kaufmann et al. 1992, Herlihy et al. 1990), thresholds were established to distinguish which sites were affected by AMD. For all sites in the Youghiogheny and North Branch Potomac River basins with ANC less than 200 μeq/l, those with sulfate concentrations greater than 500 μeq/l were designated as dominated by AMD. Sites with sulfate in the 300-500 μeq/l range were considered affected by both AMD and acidic deposition.

Ancillary field evidence of mine influence was recorded for each site in the 1995-1997 MBSS and used as an independent data set to assess the accuracy of the AMD classification. This included field observations and other known evidence of past or present mine activity or of AMD problems, as identified by the Western Maryland field crew leader (Kline 1998, personal communication). The presence of mine evidence at a site is important because it can be a source of physical degradation even where AMD does not occur. For instance, 6 sites in the Survey showed field evidence of mine influence but had ANC values > 200 μeq/l. Among the 18 sites that were classified as AMD-dominated (using water chemistry), 11 showed conclusive visual evidence of mine influence, 1 showed possible influence, and 6 showed no evidence of mine influence. Among the 15 sites that were classified as AMD and acidic deposition influenced, none showed conclusive visual evidence of mine influence, 9 showed possible influence, and 6 showed no evidence of mine influence. For those sites that were classified as AMD-dominated, sulfate concentrations ranged from 526 to 10,831 μeq/l.

To evaluate the influence of natural organic acids or fertilizers, organic anion concentrations were calculated for all sites from measured concentrations of dissolved organic carbon (DOC) and pH, using methods developed by Oliver (1983). Sites with ANC < 200 μeq/l were screened for organic acidity as the dominant source of acid influence. If organic anion concentrations at a site were greater than the total concentration of nitrate and sea-salt corrected sulfate, organic acids were considered the dominant source of acidification (Kaufmann et al. 1992). Sites with low organic anion concentrations (less than the sum of nitrate and sulfate concentrations) and high DOC values (> 8mg/l) were considered affected by both organic anions and acid deposition. This technique provides a more accurate assessment of organic acidity than is possible using DOC values alone.

High nitrate levels (especially in excess of sulfate levels) often indicate agricultural influence. All sites with ANC < 200 μeq/l were screened for agricultural influence using criteria developed specifically for the MBSS. Correlations among nitrate nitrogen concentration, upstream land use and ANC were examined for thresholds that could be used as classification criteria. A general threshold at approximately 50 percent agricultural land use was observed across Maryland, above which the concentration of nitrate increased in response to agriculture (Figure 6-5). An additional criteria for nitrate-nitrogen (NO_3-N >100 μeq/l or 1.4 mg/l) was selected based on previous assessments to exclude agricultural sites with low nitrate-nitrogen values. These criteria were combined to screen all sites with ANC < 200 μeq/l and to identify those most likely influenced by agricultural sources of acidity (Figure 6-4).

These assigned categories of acid sources were used to estimate the extent of each source affecting Maryland streams. As stated above, an estimated 28% of the total stream miles had ANC < 200 μeq/l. The extent of various acid sources are summarized in Figure 6-6. Acidic deposition was by far the most common source of acidifying compounds, being the dominant source at about 19% of stream miles. AMD was the dominant source at only 1.8% of stream miles, while an additional 1% of stream miles were likely affected by both acidic deposition and AMD. Only 0.8% were dominated by organic sources, while another 1.7% were likely affected by both organic acids and atmospheric deposition. Agriculture accounted for the acidification of 4.2% of all stream miles.

As expected, acid sources varied considerably among basins (Figures 6-6 and 6-7). In the Lower Potomac basin, for example, acidic deposition was the only source of acidity, and accounted for the acidification of 79% of stream miles. Acidic deposition was the only source of acidity in the Elk, Patuxent, and West Chesapeake basins. Ten other basins also showed evidence of acidic deposition.

Acid mine drainage was only present in the North Branch Potomac and Youghiogheny basins. In the North Branch Potomac basin, the extent of AMD effects where significant. Results indicate that 20% of stream miles in the

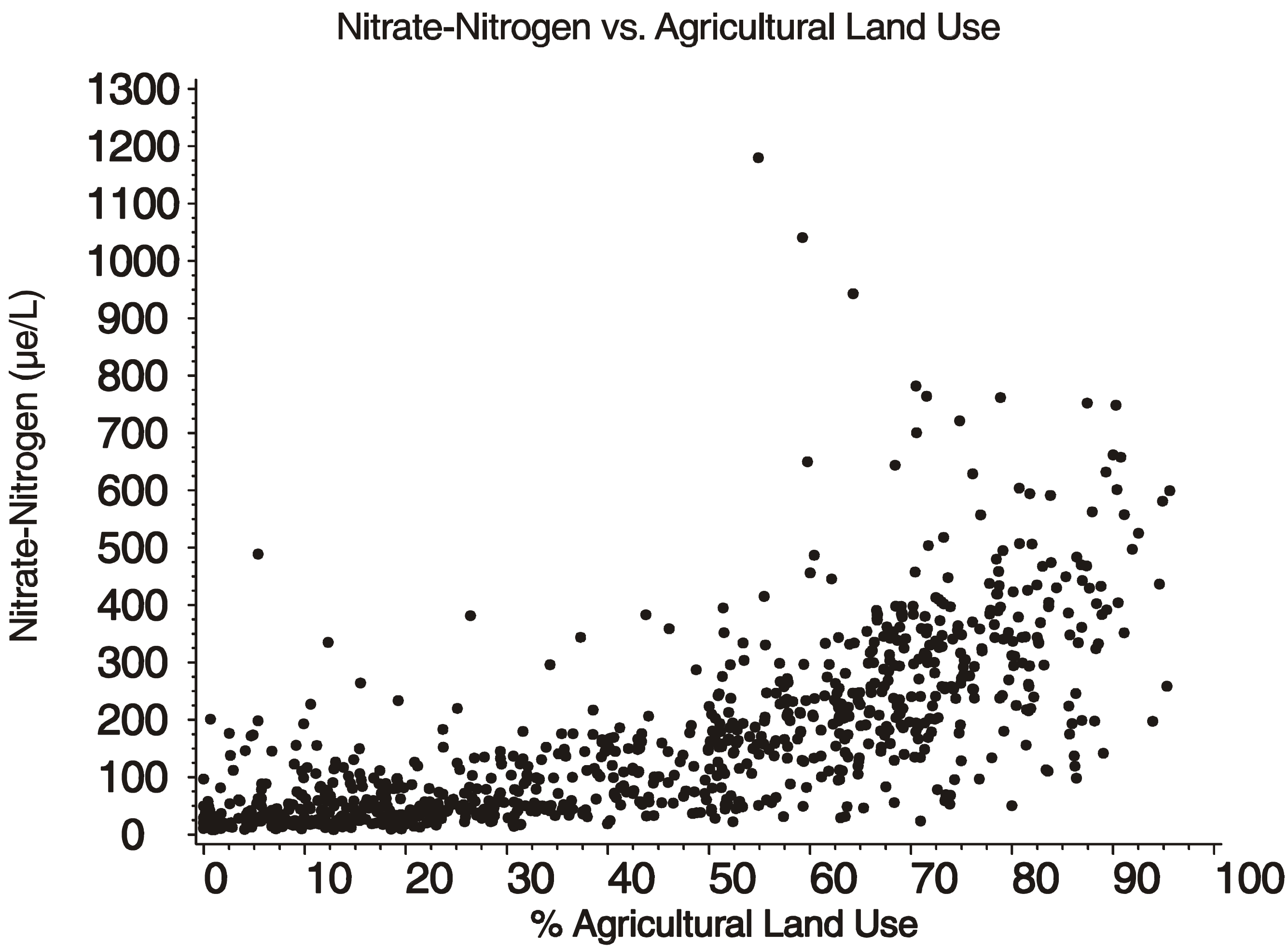

Figure 6-5. Relationship between nitrate-nitrogen (NO_3-N) and the percentage of agricultural land use for the basins sampled in the 1995-1997 MBSS

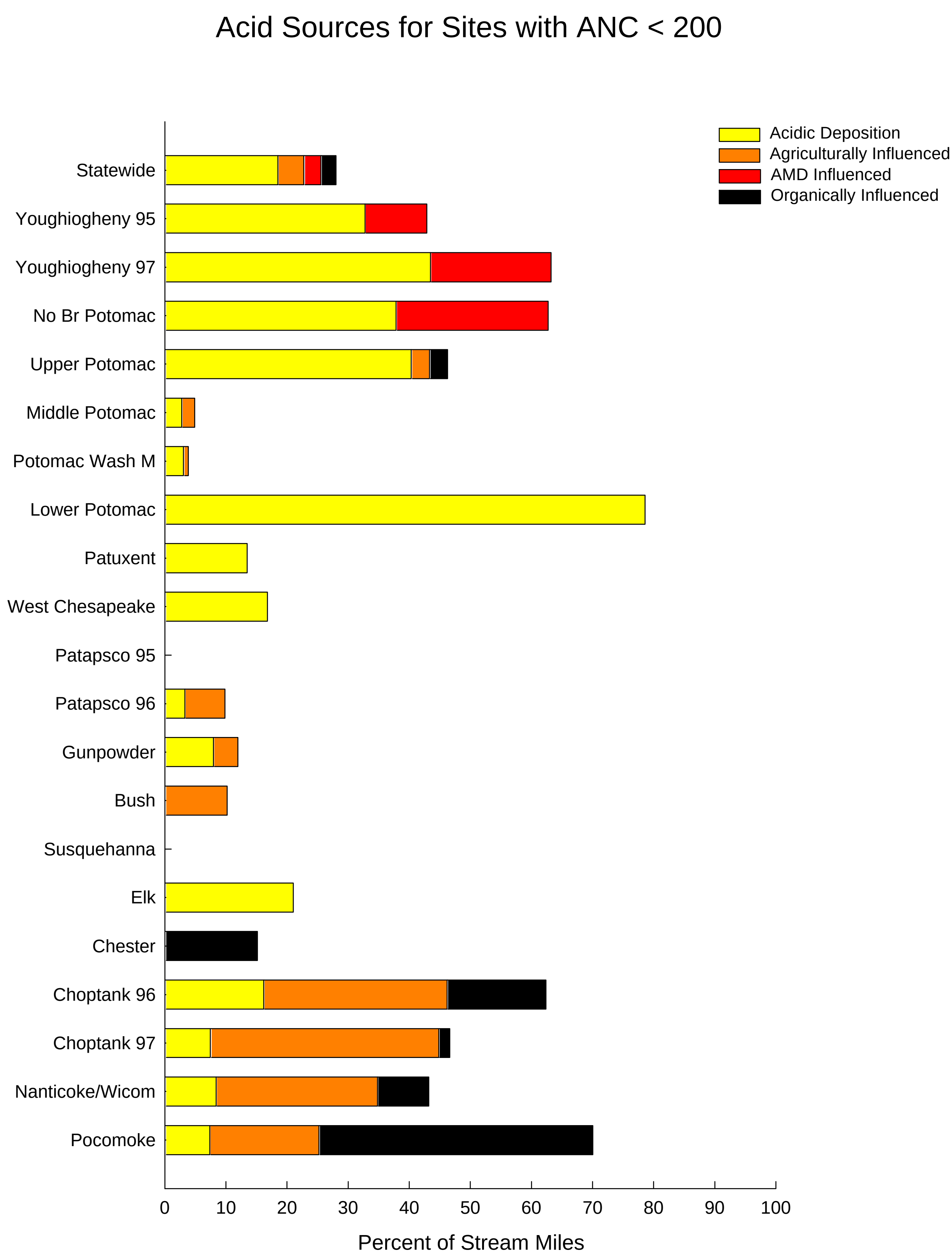

Figure 6-6. Percentage of stream miles with ANC < 200 μeq/l, by acid source for the basins sampled in the 1995-1997 MBSS. The category "AMD Influenced" includes sites affected by AMD and by both AMD and acidic deposition. The category "Organically Influenced" includes sites affected by organic sources and by both organic sources and acidic deposition.

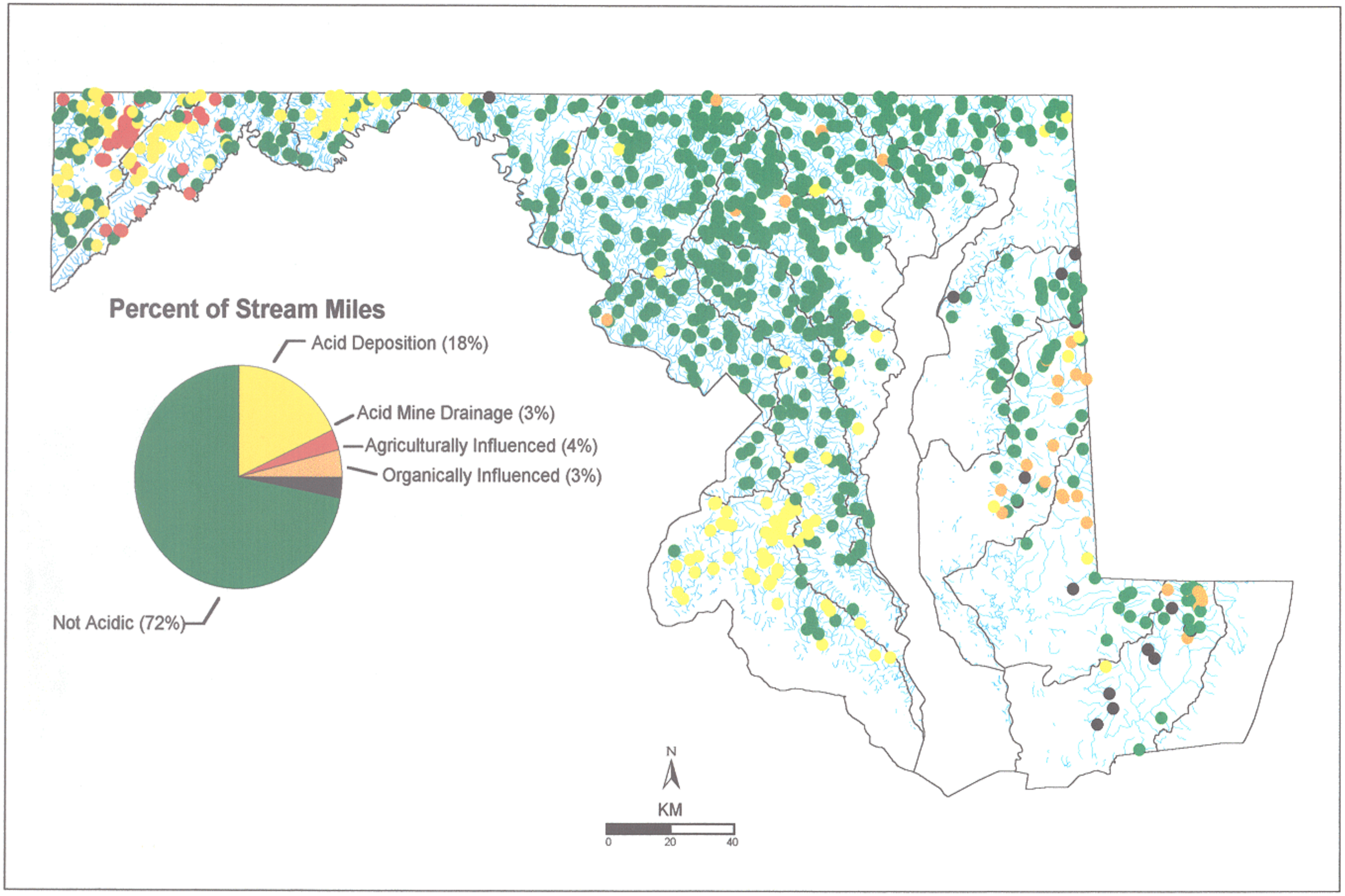

Figure 6-7. Acid sources at 1995-1997 MBSS sites

North Branch Potomac basin were affected by AMD as the dominant source, 5% were likely affected by both AMD and acidic deposition, and another 38% were dominated by acid deposition. In contrast, AMD was the dominant source for only 2% of stream miles in the Youghiogheny basin in 1995, and 11% in 1997. The combined influence of acidic deposition and AMD affected an estimated 8% of Youghiogheny stream miles in 1995 and 8% again in 1997. Another 33% of stream miles in that basin were dominated by acidic deposition in 1995, and 43% in 1997.

Statewide, only four sites (less than 1% of all stream miles) were dominated by organic sources and less than 2% of all stream miles showed combined organic and acidic deposition influences. The small number of organically dominated and influenced sites led to large standard errors (s.e. > 100%) in estimating the number of stream miles that were organically influenced. Fourteen sites had DOC > 10 mg/l, a level commonly used to characterize blackwater streams (streams rich in organic material and typically acidic due to natural sources). However, 10 of these sites had levels of nitrate and sulfate high enough to indicate a strong influence of acidic deposition. Organic anions influenced or dominated the stream chemistry of 44.7% of stream miles in the Pocomoke basin, as well as 16.2% in the Choptank, 15.1% in the Chester, and 8.4% in the Nanticoke/Wicomico basin. Organic acidification also contributed to extreme acidification (ANC < 0) in the Choptank and Pocomoke basins, but only for a small number of sites.

Across the State, 32 sites or 4.2% of acid affected stream miles were classified as agriculturally influenced. Agricultural influences on acidity were most extensive in Eastern Shore basins, accounting for 30% to 37% of stream miles in the Choptank (1996 and 1997 sampling), 26% in the Nanticoke/Wicomico, and 19% of stream miles in the Pocomoke basin. Smaller percentages were observed in the Patapsco, Bush, Gunpowder, Potomac Washington Metro, Middle Potomac, and Upper Potomac basins. Agriculture was rarely responsible for extreme acidification: only one agriculturally influenced site had an ANC < 50 μeq/l, the rest had values of 51-200 μeq/l. High nitrate concentrations were frequently accompanied by high DOC values.

The distribution of acid sources by stream order showed some differences in sources for higher order streams. The frequency of acid sources by stream order across Maryland is summarized in Figure 6-8. Acidic deposition, for example, influenced 23% of all first-order stream miles, but only 16% of all third order stream miles. Agricultural acid sources were associated with 6% of first-order stream miles, but only about 1% of second- and third-order stream miles. AMD affected about 2% of first-order and 5% of third-order stream miles. These results should be interpreted carefully: sources that occurred in less than 2% of stream miles tended to have standard errors of 100% or more.

Subpopulation analyses were done to estimate the percentage of stream miles within low ANC classes (ANC < 200 µeq/l) that were associated with each acid source. The percentage of low-ANC stream miles across the State influenced by each acid source is shown in Figure 6-9. Among streams with ANC < 200, acidic deposition was the dominant source in approximately 66% of stream miles, AMD was the dominant source in 6% of stream miles, and another 4% were affected by both acidic deposition and AMD. Agriculture accounted for the acidification of 15% of stream miles, while organic acids influenced 3% and another 6% were influenced by both organic acids and acidic deposition. Among chronically acidic streams (12 sites with ANC < 0), AMD was the dominant source in 38% of stream miles and acidic deposition was dominant in 42%. Organic acids influenced 9% of chronically acidic streams, while another 11% were influenced by both organic anions and acidic deposition. No sites with ANC < 0 were influenced by agriculture. The higher percentage of AMD-dominated stream miles reflects the presence of highly acidified sites in the North Branch Potomac and Youghiogheny basins.

In the North Branch Potomac and Youghiogheny basins, the subpopulation estimates for streams with ANC < 200 were slightly different from statewide estimates, indicating the greater prevalence of AMD in these basins. Among North Branch Potomac streams with ANC < 200, acidic deposition was the dominant source in approximately 60% of stream miles; AMD was the dominant source in 31% of stream miles; and 8% were affected by both acidic deposition and AMD. Among Youghiogheny streams sampled in 1995 with ANC < 200, acidic deposition was the dominant source in approximately 76% of stream miles; AMD was the dominant source in 5% of stream miles; and 19% were affected by both acidic deposition and AMD. Results for the Youghiogheny for 1997 were consistent with those from 1995. These results indicate that acidic deposition was by far the most common source affecting Maryland streams (ANC < 200 μeq/l), but that AMD was the source most often associated with extreme acidification (ANC < 0 μeq/l) within the North Branch Potomac and Youghiogheny basins.

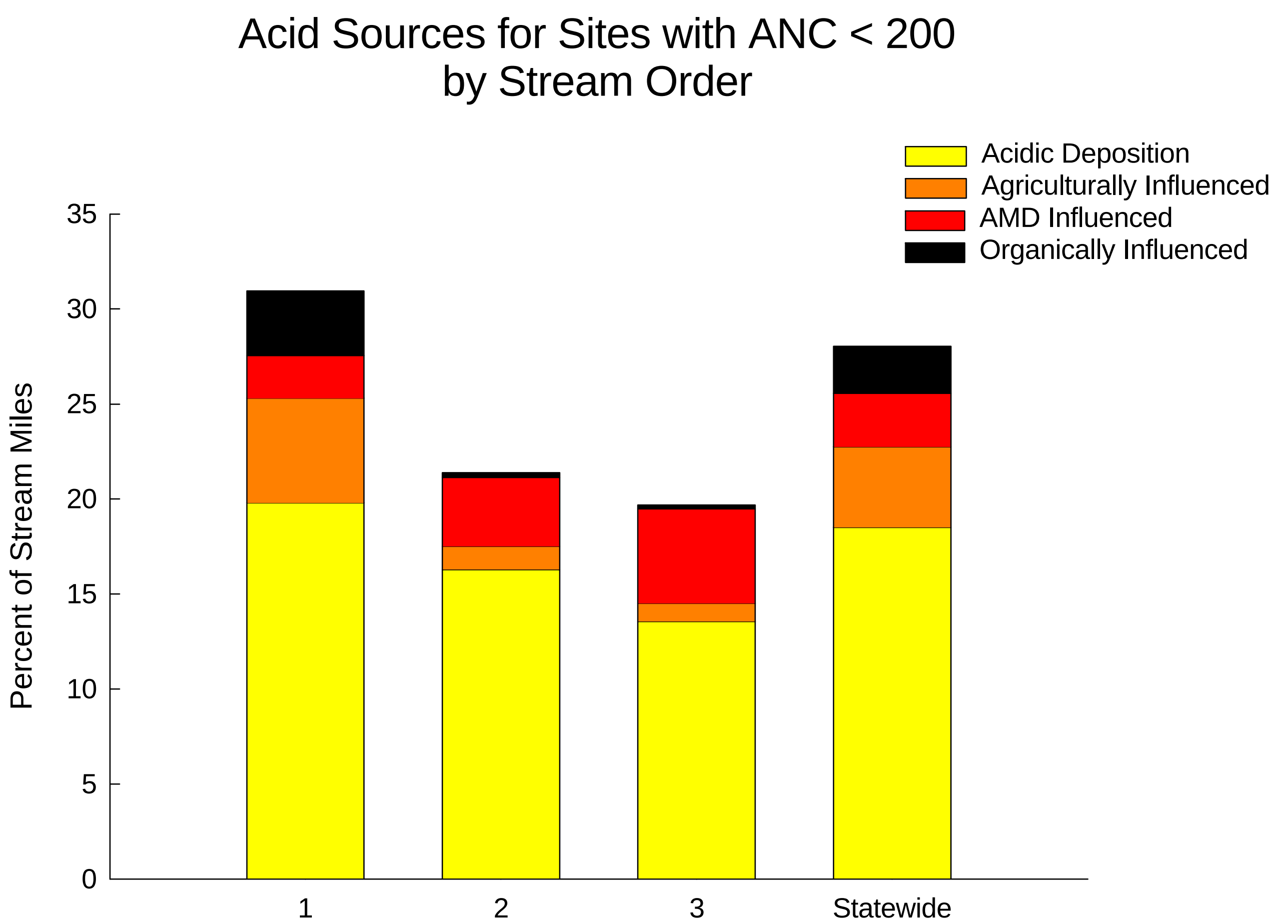

Figure 6-8. Percentage of stream miles with ANC < 200 μeq/l by acid source, by stream order for the 1995-1997 MBSS. The category "AMD Influenced" includes sites affected by AMD and by both AMD and acidic deposition. The category "Organically Influenced" includes sites affected by organic sources and by both organic sources and acidic deposition.

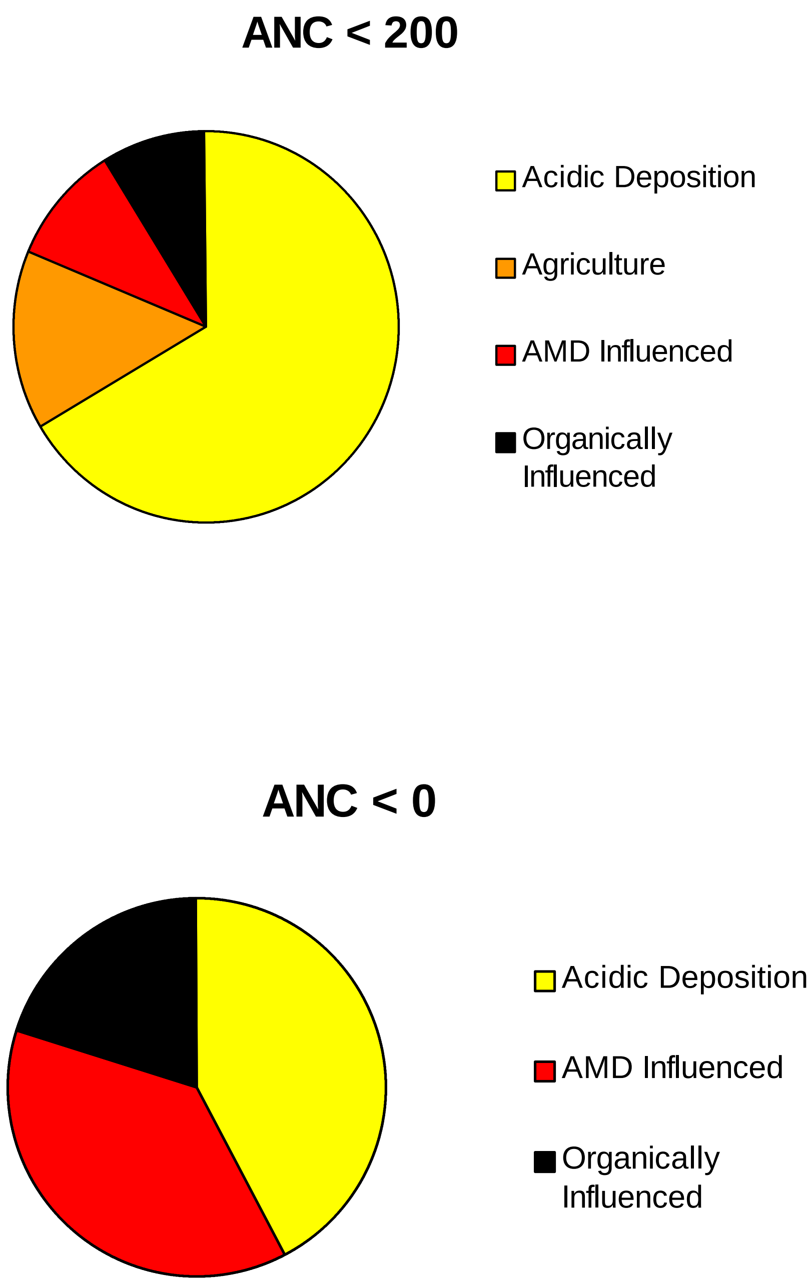

Figure 6-9. Statewide percentage of stream miles with ANC < 200 μeq/l and with ANC < 0 μeq/l by acid source. The category "AMD Influenced" includes sites affected by AMD and by both AMD and acidic deposition. The category "Organically Influenced" includes sites affected by organic sources and by both organic sources and acidic deposition.

6.4 COMPARISON WITH THE 1987 MARYLAND SYNOPTIC STREAM CHEMISTRY SURVEY

MBSS results can be compared with the previous characterization of low ANC in Maryland streams by the 1987 MSSCS (Knapp et al. 1988) (Table 6-1). The MSSCS estimated the percentage of stream miles below certain threshold levels of ANC across the entire State and within each of the State's physiographic regions. MSSCS measurements were taken in 1987, a dry year that received an average of 11% less rainfall than normal (NOAA 1987). The MSSCS estimated that the greatest concentrations of acidic or acid-sensitive streams in the State were in the Southern Coastal Plain (74% of stream miles) and the Appalachian Plateau (53%). There were some important methodological differences between the 1987 MSSCS and the 1995-1997 MBSS. For example, MSSCS sampling was conducted statewide in a single year, while MBSS basins were sampled over a three-year period. Also, the sample frame for the MSSCS specifically excluded streams known to be affected by acid mine drainage, while the MBSS did not exclude these streams. To rectify these differences, the MBSS data were re-stratified by physiographic province, excluding sites that showed AMD as a contributing source of acidity. The results of this analysis are presented in Table 6-2. Because the MSSCS was designed to provide estimates by physiographic province, standard errors are generally lower for the 1987 values. Larger error bounds around MBSS values in Table 6-2 are the result of restratification from basins to physiographic province. In two regions (Ridge and Valley, Blue Ridge), the number of sites sampled by MBSS was lower than in the 1987 survey.

Among the basins sampled in the MBSS, physiographic patterns in ANC are generally consistent with the results of the earlier MSSCS. In the MBSS (Table 6-2), sites in the Appalachian Plateau and Southern Coastal Plain had a high occurrence of acidic or acid-sensitive stream miles, comparable to findings from 1987 for these regions. This result is consistent with the low critical loads estimated for these provinces by Janicki et al., based on watershed hydrology, and the buffering abilities of vegetation, soils and bedrock. Similarly, sites in the Piedmont and the Northern Coastal Plain had a low occurrence of low ANC streams in both MSSCS and MBSS sampling, these regions are thought to have higher critical loads values. The Blue Ridge province showed a significant difference in ANC results between the MSSCS and MBSS sampling, this difference should be interpreted with caution, because the Blue Ridge is a small region and naturally has large statistical variation in results. Similarly, the Valley and Ridge province results for MBSS were noticeably different from those of the MSSCS, with relatively high standard errors (s.e. > 100%). The overall pattern, however, is broad and statistically meaningful. Across all provinces, the MBSS results show a lower percentage of low ANC sites than do the MSSCS results (from 33% to 26%). This suggests a genuine improvement in the condition of Maryland streams from 1987 to 1997.

6.5 ASSOCIATIONS BETWEEN ACIDIFICATION AND BIOLOGICAL CONDITION

Biological data for sites within designated pH and ANC classes were compared to investigate the relationship between acidic conditions (primarily acidic deposition, as explained above) and stream communities. Acidification of streams may cause declines in the biotic integrity of fish assemblages, as a result of the loss of species sensitive to acidification, increases in acid-tolerant species, or the total elimination or reduction in abundance of biota.

Streams sensitive to acidification may experience intermittent periods of low pH which may be harmful to fish populations. In particular, streams may be subject to episodic acidification during springtime, when larval and juvenile fish are particularly vulnerable to adverse changes in water quality. The MBSS study design did not focus on sampling during high stream flow events that could have produced low pH episodes. Instead, the MBSS results corroborate a causal relationship between the potential for episodic acidification and loss of biotic integrity. The MBSS also documented a reduction in abundance and species richness in low ANC streams.

The fish IBI (see Chapter 5) integrates a number of attributes of the fish community, providing a quantitative biological indicator calibrated against reference conditions. A review of IBI scores shows a decline at low pH sites (Figure 6-10) with IBI scores dropping into the poor range at a pH between 5 and 6. Streams sensitive to acidification may experience episodic acidification and even intermittent periods of low pH may be harmful to fish populations. The MBSS results are merely a snapshot of acidity and biological condition at one point in time. The transient nature of episodic acidity and the temporal and spatial heterogeneity of fish populations both contribute to variability and uncertainty in the relationship between pH and fish IBI.

Observed associations between acidity and the fish IBI were paralleled by similar relationships between acidity and other characteristics of the fish community, including species richness and biomass. Among the basins sampled in the 1995-1997 MBSS, fish species richness (mean number of species per stream segment) was significantly lower at sites

Table 6-1. Percentage of acidic and acid-sensitive stream miles, as estimated by the 1987 Maryland Synoptic Stream Chemistry Survey (MSSCS). Estimates are the percentage of stream miles below threshold ANC values, by physiographic region.

ANC (μeq/l)	PHYSIOGRAPHIC REGION													
	Appalachian Plateau		**Valley and Ridge**		**Blue Ridge**		**Piedmont**		**Northern Coastal Plain**		**Southern Coastal Plain**		**All**	
	n = 139		**n = 47**		**n = 50**		**n = 125**		**n = 99**		**n = 99**		**n = 559**	
	Percent	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**
<0	10.7	3.6	0	0	0	0	0	0	2.1	1.5	7.6	2.9	3.6	0.9
<50	15.7	3.9	0	0	5.8	2.5	0.9	1.0	4.7	2.8	29.3	4.7	10.0	1.4
<200	53.3	4.6	1.5	1.3	26.0	5.7	8.9	3.6	28.3	5.2	74.4	5.0	33.4	2.2

Table 6-2. Percentage of acidic and acid-sensitive stream miles, as estimated by the 1995-1997 Maryland Biological Stream Survey (MBSS). Estimates are the percentage of stream miles below threshold ANC values, by physiographic region.

ANC (μeq/l)	PHYSIOGRAPHIC REGION													
	Appalachian Plateau		**Valley and Ridge**		**Blue Ridge**		**Piedmont**		**Northern Coastal Plain**		**Southern Coastal Plain**		**All**	
	n = 197		**n - 24**		**n = 11**		**n = 385**		**n = 204**		**n = 138**		**n = 954**	
	Percent	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**	**Percent**	**Std. Error**
<0	3.4	6.8	0	0	0	0	0	0	0.6	1.3	4.9	6.2	1.4	1.5
<50	6.4	12.3	8.2	14.7	0	0	0	0	2.4	3.3	16.9	8.1	5.0	3.5
<200	53.3	20.3	16.4	19.5	0	0	5.6	4.8	19.2	11.3	63.6	0	25.9	3.4

*Variance statistically undefined

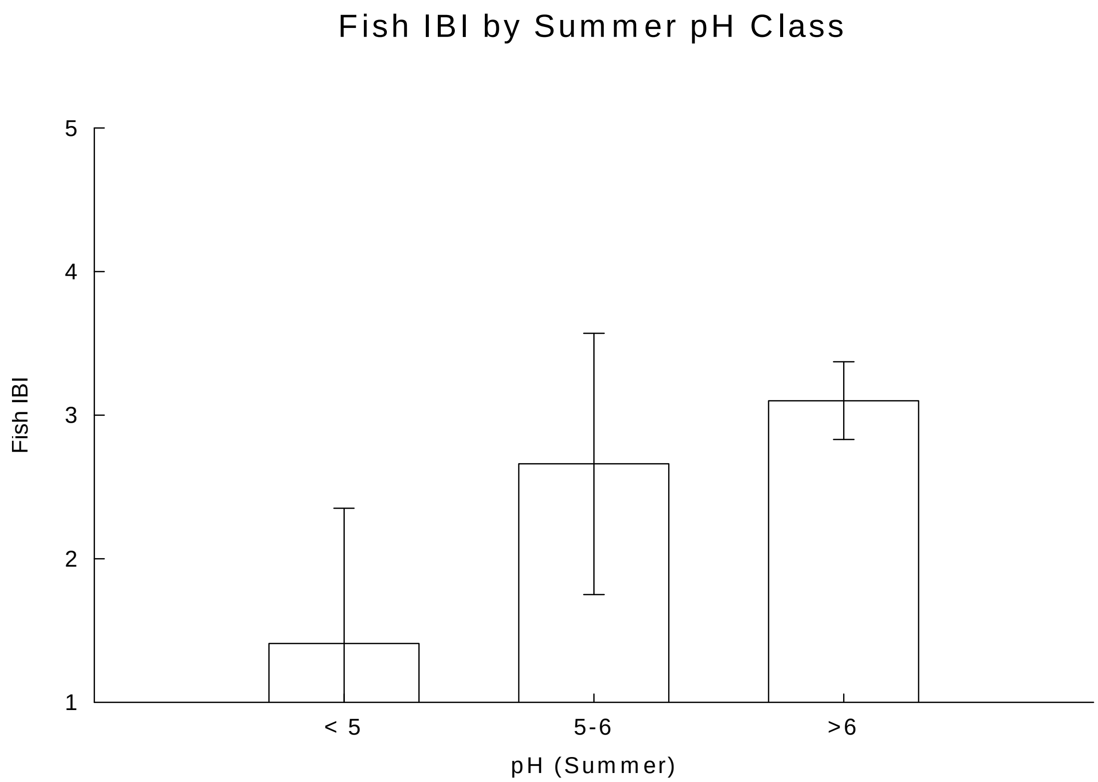

Figure 6-10. Fish IBI by summer pH class (< 5, 5-6, > 6) for the 1995-1997 MBSS

sensitive to acidification (ANC 50-200 μeq/l) than where ANC values were higher (>200 μeq/l) (Figure 6-11). For sites with ANC < 0, fish species richness was severely diminished.

Fish biomass also varied with ANC. Statewide, total fish biomass decreased dramatically in ANC class 50-200, compared to ANC class > 200 (Figure 6-12). Total fish biomass in ANC class 0-50 was less than half than that in ANC class 50-200. Gamefish do not persist where ANC is < 0, therefore their biomass drops to zero in that class.

Other biological communities such as macroinvertebrates and amphibians and reptiles may offer additional clues to help detect the impacts of acidification. Two measures of the benthic macroinvertebrate community, the benthic IBI and the Hilsenhoff Biotic Index (Chapter 5), were compared among ANC classes. The benthic IBI combines several measures of the abundance and diversity of benthic macroinvertebrate organisms. Since benthic communities are sedentary, they tend to experience the integrated effects of chronic and episodic acidification over many seasons. Thus, the benthic IBI may be a valuable indicator of the effects of chronic acidification in Maryland streams. It is not surprising that the benthic IBI decreases strongly with low pH; and passes into the "very poor" rating for pH < 5 (Figure 6-13). Because benthos are relatively immobile, the benthic IBI is intrinsically less uncertain than the fish IBI and is probably a more reliable indicator of the effects of chronic acidification.

A comparison between benthic and fish IBI scores by ANC class reveals similar results (Figure 6-14). Both indices decrease with low ANC and are "very poor" for ANC < 0. It is not clear why IBI scores are higher for ANC 50-200 than for ANC > 200. However, it is important to note that this analysis only considers the effects of acidification on biological condition; many other anthropogenic and natural factors affect IBI scores and may have confounding effects on this analysis.

The Hilsenhoff Biotic Index, which increases with the presence of pollution-tolerant macroinvertebrate species, was highest at sites with 0-50 μeq/l (Hilsenhoff = 5.1). The average value of the index was lowest for sites with ANC < 0 (Hilsenhoff = 3.9). This may be indicate that the Hilsenhoff Biotic Index (originally developed to detect organic pollution) is not well suited to detecting acidification.

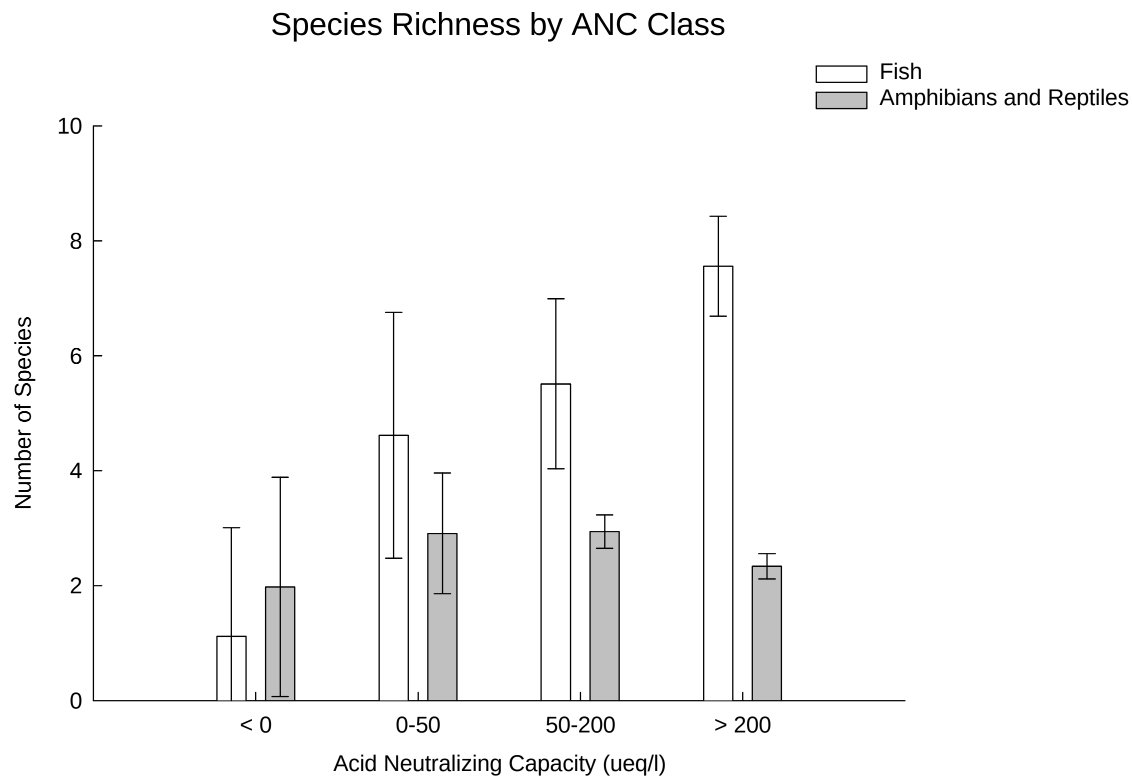

Figure 6-11. Fish and amphibian and reptile species richness by ANC class (< 0, 0-50, 50-200, > 200 μeq/l) for the 1995-1997 MBSS

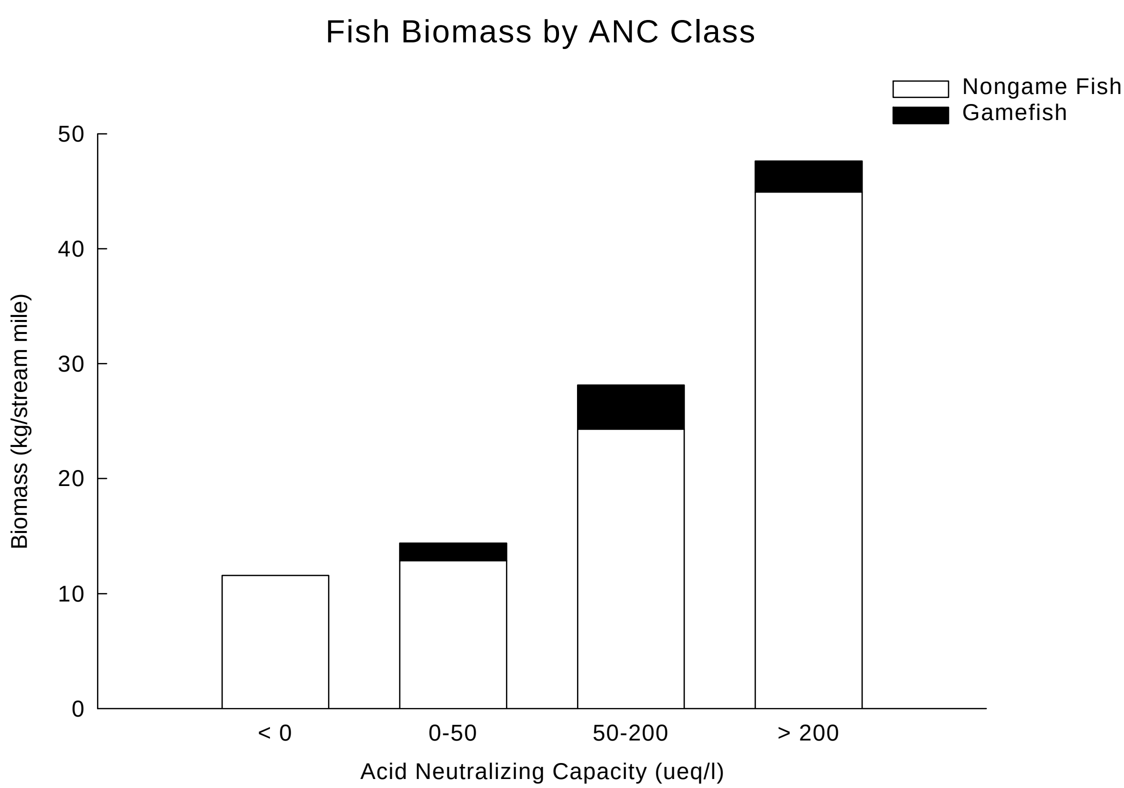

Figure 6-12. Statewide biomass estimates (kg/stream mile) for nongame fish and gamefish by ANC class(< 0, 0-50, 50-200, > 200 μeq/l), 1995-1997 MBSS

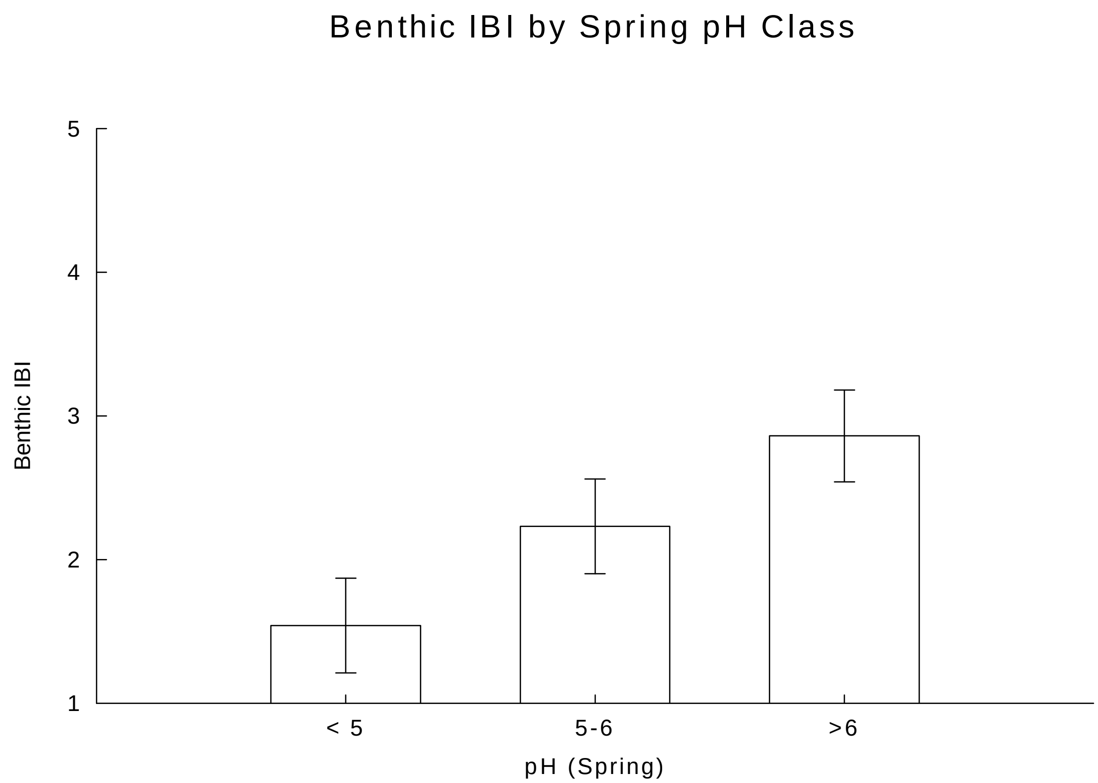

Figure 6-13. Benthic IBI by spring pH class (< 5, 5-6, > 6) for the 1995-1997 MBSS

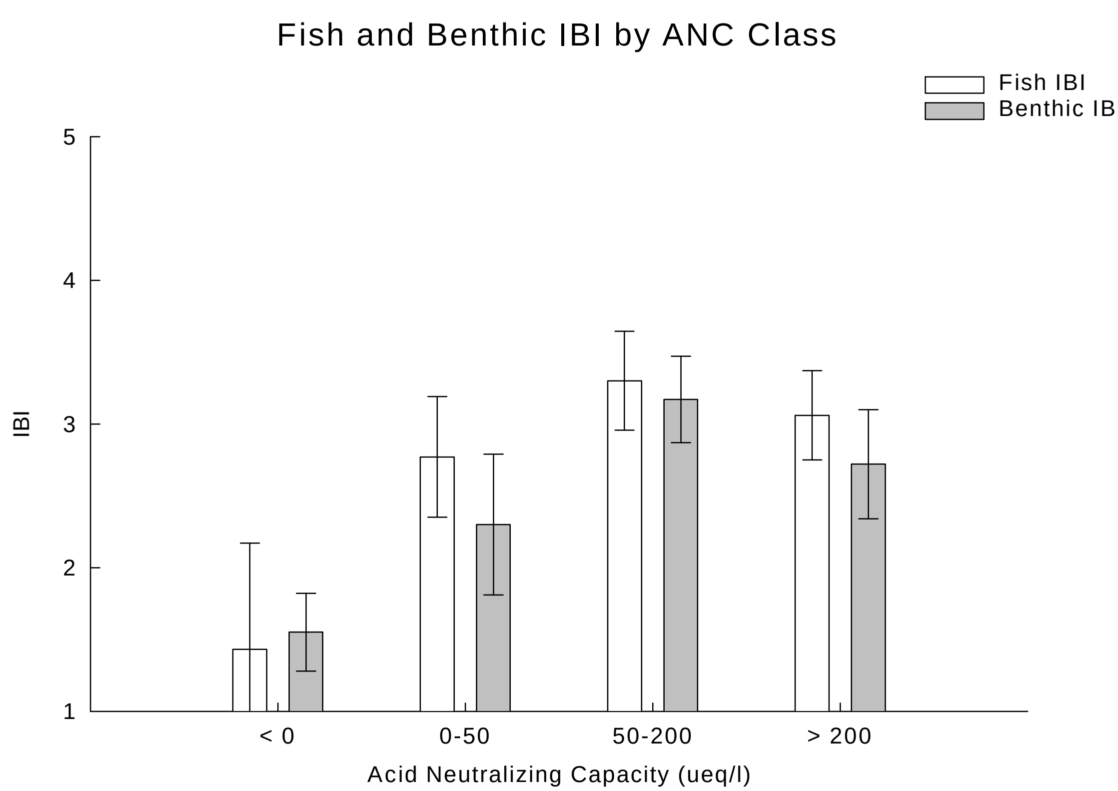

Figure 6-14. Fish and benthic IBI by ANC class (< 0, 0-50, 50-200, > 200 μeq/l) for the 1995-1997 MBSS

Table 6-3. Fish species found at 1995-1997 MBSS sites with summer pH < 6.5				
	pH < 5.0	**pH 5.0 - 5.5**	**pH 5.5 - 6.0**	**pH 6.0 - 6.5**
Least brook lamprey		X	X	X
Sea lamprey			X	X
American eel		X	X	X
Chain pickerel				
Redfin pickerel		X	X	X
	X	X	X	X
Eastern mudminnow				
	X	X	X	X
Blacknose dace				
Bluntnose minnow			X	X
Central stoneroller				X
Common shiner				X
Creek chub				X
Cutlips minnow			X	X
Fallfish			X	X
Golden shiner		X	X	X
Ironcolor shiner			X	X
Longnose dace				X
River chub			X	X
Rosyface shiner				X
Rosyside dace				X
Satinfin shiner		X	X	X
Spotfin shiner				X
Spottail shiner				X
Swallowtail shiner				X
			X	X
Creek chubsucker				
Northern hogsucker		X	X	X
White sucker				X
			X	X
Brown bullhead				
Margined madtom			X	X
Tadpole madtom			X	X
Yellow bullhead		X	X	X
			X	X
Brook trout				
Brown trout			X	X
				X
Pirate perch	X			
			X	X
Banded killifish				
Mosquitofish				X
				X

Table 6-3. Cont'd				
	pH < 5.0	**pH 5.0 - 5.5**	**pH 5.5 - 6.0**	**pH 6.0 - 6.5**
Mottled sculpin			X	X
Potomac sculpin			X	X
Banded sunfish	X	X		X
Black crappie				X
Bluegill		X	X	X
Bluespotted sunfish	X	X	X	X
Flier				X
Green sunfish			X	X
Largemouth bass			X	X
Mud sunfish	X			X
Pumpkinseed		X	X	X
Redbreast sunfish			X	X
Rock bass				X
Smallmouth bass				X
Warmouth		X	X	X
Fantail darter			X	X
Greenside darter				X
Shield darter				X
Swamp darter			X	X
Tessellated darter		X	X	X
Yellow perch				X
Total Number of Species	**6**	**15**	**34**	**56**

Another measure of biological condition available from MBSS data is the species richness of amphibians and reptiles. Species richness was slightly less at ANC < 0 μeq/l, but showed no significant differences for sites with higher ANC values (Figure 6-11). The differences among classes were not large (a difference of about one species) and may be indicative of factors other than water quality (e.g., the condition of the riparian corridor).

6.6 FISH TOLERANCE TO LOW PH CONDITIONS

A breakdown of fish species composition at low pH sites was examined to determine which species were most tolerant of acidic conditions. The results are shown in Table 6-3. Many of these species have been previously reported as tolerant to low pH conditions (Graham 1993, Baker and Christensen 1991), although not all Maryland fish species were covered by these earlier studies. For the most part, these fish species sampled in the 1995-1997 MBSS were present at pH conditions within previously reported ranges of acid tolerance.

6.7 FISH ABUNDANCE UNDER ACIDIFIED OR ACID-SENSITIVE CONDITIONS

The estimated density of fish (mean number of fish per stream mile) varied under acidified and acid-sensitive conditions. Statewide estimates were calculated for the number of individual fish per stream mile within each of four ANC classes (< 0, 0-50, 50-200, > 200 μeq/l). Estimates reported here were not adjusted for capture efficiency. Across all sites, the number of fish per stream mile declined with low ANC. Only 43% of sites sampled in summer with ANC < 0 μeq/l had fish. In contrast, 91% of the summer sites with ANC of 0-50 μeq/l had fish.

To investigate differences in the abundance of individual fish species, the density of fish within each ANC class was calculated (Table 6-4). Five species of fish were found in all four of the ANC classes: redfin pickerel (*Esox americanus*), eastern mudminnow (*Umbra pygmaea*), pirate perch (*Aphredoderus sayanus*), banded sunfish (*Enneacanthus obesus*), and bluespotted sunfish (*Enneacanthus gloriosus*). The mud sunfish (*Acantharchus pomotis*) was found at sites in every ANC class except 0-50.

Dramatic differences were seen in fish species composition and abundance above and below the threshold for acid sensitivity (ANC = 200 μeq/l). Seventeen species found at sites with ANC > 200 were absent from sites with ANC < 200, while only one species found at ANC < 200 was absent at sites with higher ANC. In addition, 44 species decreased in abundance at ANC 50-200 (as compared to ANC > 200). The average loss between these two ANC classes was 135 fish per stream mile. The species exhibiting the greatest declines were blacknose dace (*Rhinichthys atratulus*; 1,377 fish per stream mile), mottled sculpin (*Cottus bairdi*; 435), rosyside dace (*Clinostomus funduloides;* 464), bluntnose minnow (*Pimephales notatus*; 339) and creek chub (*Semotilis atromaculatus*; 418). Interestingly, some of these species are commonly considered tolerant of human impacts in regions where acidification is not prevalent. Twenty-one species were more abundant at ANC 50-200 than at ANC > 200, but the average increase (41 fish per stream mile) was not large enough to offset the observed declines in other species.

Differences were also seen in fish species composition and abundance between the ANC classes of 50-200 and 0-50. Forty-seven species decreased in abundance at ANC 0-50 (as compared to 50-200). The average loss between these two classes was 85 fish. The species exhibiting the greatest declines were least brook lamprey (*Lampetra aepyptera*), eastern mudminnow, and mottled sculpin. Because lampreys spend up to 7 years as larvae in streams, they may be particularly sensitive to acidic episodes.

Between the ANC classes of 0-50 and < 0, 32 species decreased in abundance at ANC < 0. The density of 30 of these species went to zero when the ANC value was < 0, indicating their intolerance to extreme acidification. The two remaining species - pirate perch and bluespotted sunfish - persisted at sites with high levels of acidification. Four species of fish actually increased in abundance in the ANC < 0 category. These fish were the redfin pickerel, eastern mudminnow, banded sunfish, and mud sunfish. This result indicates that these species are acid-tolerant, consistent with reported tolerance levels (Baker and Christensen 1991; Jenkins and Burkland 1993) and may be outcompeted by less tolerant species in streams with higher ANC values.

Given that an estimated 28% of stream miles in the study area (about 2240 miles) had ANC less than 200 μeq/l, the effects of acidification on many fish populations appear to be significant. It is important to note that this analysis considered only acidification, not other natural or anthropogenic effects on fish abundance. In particular, geographic differences may be responsible for some of the differences observed here. For example, brook trout tend to favor the high-gradient streams of Western Maryland, where ANC conditions < 200 are more common. This geographic difference would explain the apparent increase in brook trout abundance in streams with ANC 50-200, compared to streams in other parts of the state that have ANC > 200 but lack suitable habitat for brook trout.

Table 6-4. Mean number of individual fish per stream mile within each acid neutralizing capacity (ANC) class by species, 1995-1997 MBSS

SPECIES	ANC (ueq/l)							
	< 0		0 -50		50-200		> 200	
	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error
American brook lamprey	0.00	0.00	0.00	0.00	0.07	0.08	39.80	87.58
Least brook lamprey	0.00	0.00	10.33	16.01	331.78	311.02	62.21	41.35
Sea lamprey	0.00	0.00	1.02	1.66	10.09	10.16	8.59	6.95
Longnose gar	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00
American eel	0.00	0.00	159.89	264.88	196.57	186.30	181.44	112.35
Gizzard shad	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.04
Chain pickerel	0.00	0.00	13.52	21.48	33.07	33.67	2.36	1.46
Redfin pickerel	1426.31	3142.75	97.43	157.97	99.54	100.76	48.46	32.40
Eastern mudminnow	5563.91	11783.22	921.53	1448.92	1460.11	1437.77	1473.07	1211.74
Blacknose dace	0.00	0.00	674.66	1154.61	882.63	853.80	2259.67	1415.02
Bluntnose minnow	0.00	0.00	0.00	0.00	20.53	32.53	359.15	222.13
Central stoneroller	0.00	0.00	0.00	0.00	9.28	9.70	230.88	145.65
Comely shiner	0.00	0.00	0.00	0.00	0.00	0.00	0.80	0.60
Common carp	0.00	0.00	0.00	0.00	0.00	0.00	0.69	0.63
Common shiner	0.00	0.00	0.00	0.00	9.57	10.11	159.33	130.44
Creek chub	0.00	0.00	138.73	222.80	328.31	333.04	745.86	469.55
Cutlips minnow	0.00	0.00	0.00	0.00	17.94		117.34	72.19
Eastern silvery minnow	0.00	0.00	0.00	0.00	0.17	0.19	5.81	4.08
Fallfish	0.00	0.00	24.86	39.19	82.63	77.08	75.97	*
Fathead minnow	0.00	0.00	0.00	0.00	1.83	2.93	104.70	137.44
Golden shiner	0.00	0.00	102.28	177.72	81.46	83.63	65.88	43.83
Goldfish	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.11
Ironcolor shiner	0.00	0.00	0.00	0.00	1.55	1.49	0.17	0.24
Longnose dace	0.00	0.00	1.25	2.36	88.76	88.39	390.16	246.72
Pearl dace	0.00	0.00	821.26	1465.65	0.00	0.00	68.57	62.32
River chub	0.00	0.00	34.21	86.85	3.36	3.44	51.89	*
Rosyface shiner	0.00	0.00	0.00	0.00	0.00	0.00	4.21	2.75
Rosyside dace	0.00	0.00	69.64	107.39	127.82	119.43	591.47	383.16
Satinfin shiner	0.00	0.00	0.00	0.00	2.63	2.94	47.02	33.91
Silverjaw minnow	0.00	0.00	0.00	0.00	0.00	0.00	14.14	9.43
Spotfin shiner	0.00	0.00	0.00	0.00	0.00	0.00	11.84	8.23
Spottail shiner	0.00	0.00	0.00	0.00	16.55	16.33	117.30	428.03
Striped shiner	0.00	0.00	0.00	0.00	3.70	6.09	1.40	2.34
Swallowtail shiner	0.00	0.00	0.00	0.00	11.39	14.45	207.01	193.80
Creek chubsucker	0.00	0.00	30.49	47.65	142.03	136.79	94.77	64.96
Golden redhorse	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Northern hogsucker	0.00	0.00	0.00	0.00	3.41	4.51	44.23	27.66
Shorthead redhorse	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.06
White sucker	0.00	0.00	25.83	41.03	106.39	100.34	416.13	264.01
Brown bullhead	0.00	0.00	2.65	4.32	188.33	276.05	50.06	32.04
Channel catfish	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01
Margined madtom	0.00	0.00	10.22	16.86	59.01		85.16	53.09

Table 6-4. Cont'd

SPECIES	ANC (ueq/l)							
	< 0		0 -50		50-200		> 200	
	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error
Tadpole madtom	0.00	0.00	1.54	2.43	80.73	98.04	43.34	33.43
White catfish	0.00	0.00	0.00	0.00	0.06	0.08	0.03	0.02
Yellow bullhead	0.00	0.00	9.29	19.84	3.74	4.59	23.61	14.98
Brook trout	0.00	0.00	73.29	153.72	128.64	129.37	26.71	19.54
Brown trout	0.00	0.00	0.00	0.00	6.88	7.55	36.79	24.65
Cutthroat trout	0.00	0.00	0.00	0.00	0.18	0.17	0.02	0.04
Rainbow trout	0.00	0.00	1.50	3.14	0.89	0.89	1.33	0.93
Pirate perch	58.22	130.62	72.46	114.46	198.27	198.78	145.90	211.77
Banded killifish	0.00	0.00	0.00	0.00	0.38	0.39	23.69	17.62
Mummichog	0.00	0.00	0.00	0.00	0.00	0.00	62.58	53.78
Mosquitofish	0.00	0.00	0.00	0.00	0.49	0.50	6.17	5.40
Checkered sculpin	0.00	0.00	310.01	553.25	0.00	0.00	88.36	166.50
Mottled sculpin	0.00	0.00	51.76	106.24	1046.59	1101.35	1481.42	1030.66
Potomac sculpin	0.00	0.00	0.00	0.00	137.66	146.59	279.25	173.26
Striped bass	0.00	0.00	0.00	0.00	0.00	0.00	0.56	0.91
White perch	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.07
Banded sunfish	396.20	878.11	17.84	31.49	4.93	5.54	2.87	2.55
Black crappie	0.00	0.00	0.00	0.00	9.93	10.12	1.33	1.00
Bluegill	0.00	0.00	17.83	28.65	160.98	155.83	170.36	106.22
Bluespotted sunfish	14.55	32.14	171.38	268.46	43.81	50.72	57.68	39.15
Flier	0.00	0.00	0.00	0.00	0.95	0.95	0.00	0.00
Green sunfish	0.00	0.00	0.79	1.29	1.76	1.78	113.06	80.96
Largemouth bass	0.00	0.00	0.26	0.42	10.50	10.25	62.49	55.66
Longear sunfish	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.04
Mud sunfish	6.47	14.51	0.00	0.00	0.46	0.49	0.44	0.34
Pumpkinseed	0.00	0.00	27.37	44.91	71.01	68.37	86.66	54.67
Redbreast sunfish	0.00	0.00	4.65	9.92	48.63	45.67	93.52	58.44
Rock bass	0.00	0.00	0.25	0.56	11.62	12.78	10.13	6.79
Smallmouth bass	0.00	0.00	3.01	6.54	1.09	1.16	7.61	4.83
Warmouth	0.00	0.00	3.24	5.19	11.14	10.53	0.06	0.05
Fantail darter	0.00	0.00	0.00	0.00	38.93	37.15	168.30	106.15
Glassy darter	0.00	0.00	0.00	0.00	2.05	2.10	0.43	0.38
Greenside darter	0.00	0.00	0.00	0.00	2.13	2.36	22.71	*
Johnny darter	0.00	0.00	0.00	0.00	47.57	61.61	2.03	3.33
Logperch	0.00	0.00	0.00	0.00	0.00	0.00	1.81	1.84
Rainbow darter	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.02
Shield darter	0.00	0.00	0.00	0.00	1.52	2.59	16.14	20.54
Stripeback darter	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.10
Swamp darter	0.00	0.00	4.23	7.34	0.21	0.22	1.58	1.26
Tessellated darter	0.00	0.00	64.58	102.81	204.47	197.40	514.91	414.64
Yellow perch	0.00	0.00	7.93	13.99	24.91	41.50	2.64	1.85
Total Number of Species	**6**		**38**		**64**		**81**	